

CLAIMS

Sep 15
1. A titanium catalyst for reaction between a carbon-carbon unsaturated bond and a compound having an electrophilic functional group or an electrophilic reagent, said titanium catalyst being composed of a titanium compound represented by the formula (1) below



(where X^1 , X^2 , X^3 , and X^4 denote independently a halogen atom, C_{1-20} alkoxy group, aralkyloxy group, aryloxy group, or $-\text{NRxRy}$ group (where Rx and Ry denote independently a C_{1-20} alkyl group or aralkyl group), and any two of X^1 , X^2 , X^3 , and X^4 may form a ring.) and a Grignard reagent represented by the formula (2) below in a molar amount 1-10 times as much as the titanium compound.



(where R^1 denotes a C_{2-10} alkyl group having a hydrogen atom at the β position and X^5 denotes a halogen atom.)

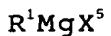
2. The titanium catalyst as defined in Claim 1, wherein the titanium compound is one which has an asymmetric ligand.

3. A process for producing a titanium catalyst for reaction between a carbon-carbon unsaturated bond and a compound having an electrophilic functional group or an electrophilic reagent, said process comprising reacting a titanium compound represented by the formula (1) below



(where X^1 , X^2 , X^3 , and X^4 denote independently a halogen atom, C_{1-20} alkoxy group, aralkyloxy group, aryloxy group, or $-\text{NRxRy}$ group (where Rx and Ry denote independently a C_{1-20} alkyl group or aralkyl group), and any two of X^1 , X^2 , X^3 , and X^4 may form a ring.) with a Grignard reagent represented by the formula (2)

below in a molar amount 1-10 times as much as the titanium compound.

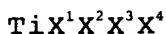


(2)

(where R^1 denotes a C_{2-10} alkyl group having a hydrogen atom at the β position and X^5 denotes a halogen atom.)

4. The titanium catalyst as defined in Claim 3, wherein the titanium compound is one which has an asymmetric ligand.

10 5. An organotitanium reacting reagent which is composed of a titanium compound represented by the formula (1) below



(1)

15 (where X^1 , X^2 , X^3 , and X^4 denote independently a halogen atom, C_{1-20} alkoxy group, aralkyloxy group, aryloxy group, or $-NR_xR_y$ group (where R_x and R_y denote independently a C_{1-20} alkyl group or aralkyl group), and any two of X^1 , X^2 , X^3 , and X^4 may form a ring.), a Grignard reagent represented by the formula (2) below in a molar amount 1-10 times as much as the titanium compound,



(2)

20 (where R^1 denotes a C_{2-10} alkyl group having a hydrogen atom at the β position and X^5 denotes a halogen atom.), and a compound having a carbon-carbon unsaturated bond.

25 6. The organotitanium reacting agent as defined in Claim 4, wherein the titanium compound is one which has an asymmetric ligand.

30 7. The organotitanium reacting reagent as defined in Claim 5 or 6, wherein the compound having a carbon-carbon unsaturated bond is any of olefin compounds, acetylene compounds, or allene compounds.

8. A process for producing an organotitanium reacting reagent, said process comprising reacting together a titanium compound represented by the formula (1) below



(where X^1 , X^2 , X^3 , and X^4 denote independently a halogen atom, C_{1-20} alkoxy group, aralkyloxy group, aryloxy group, or $-NR_xR_y$ group (where R_x and R_y denote independently a C_{1-20} alkyl group or aralkyl group), and any two of X^1 , X^2 , X^3 , and X^4 may form a ring.), a Grignard reagent represented by the formula (2) below in a molar amount 1-10 times as much as the titanium compound,



(where R^1 denotes a C_{2-10} alkyl group having a hydrogen atom at the β position and X^5 denotes a halogen atom.), and a compound having a carbon-carbon unsaturated bond.

9. The process as defined in Claim 8, wherein the titanium compound is one which has an asymmetric ligand.

10. The process as defined in Claim 8 or 9, wherein the compound having a carbon-carbon unsaturated bond is any of olefin compounds, acetylene compounds, or allene compounds.

11. A process for addition reaction which comprises performing addition reaction on a compound having a carbon-carbon unsaturated bond and a compound having an electrophilic functional group or an electrophilic reagent, in the presence of a titanium compound represented by the formula (1) below



(where X^1 , X^2 , X^3 , and X^4 denote independently a halogen atom, C_{1-20} alkoxy group, aralkyloxy group, aryloxy group, or $-NR_xR_y$ group (where R_x and R_y denote independently a C_{1-20} alkyl group

or aralkyl group), and any two of X^1 , X^2 , X^3 , and X^4 may form a ring.) and a Grignard reagent represented by the formula (2) below in a molar amount 1-10 times as much as the titanium compound,

$$R^1MgX^5$$

(2)

(where R¹ denotes a C₂₋₁₀ alkyl group having a hydrogen atom at the β position and X⁵ denotes a halogen atom.)

12. A process for addition reaction which comprises adding to the organotitanium reacting reagent defined in Claim 5 a compound having an electrophilic functional group or an electrophilic reagent, thereby performing addition reaction on a compound having a carbon-carbon unsaturated bond in the presence of said organotitanium reacting agent.

13. The process as defined in Claim 11 or 12, wherein the reaction between a compound having an electrophilic functional group and a compound having a carbon-carbon unsaturated bond is followed by further addition of a compound having an electrophilic functional group.

14. The process as defined in Claim 11, ~~12 or 13~~, wherein
the reaction between a compound having an electrophilic
functional group and a compound having a carbon-carbon
unsaturated bond is followed by addition of an electrophilic
reagent.

15. The process for addition reaction as defined in Claim 11, wherein the compound having a carbon-carbon unsaturated bond and the compound having an electrophilic functional group are replaced by a compound having both a carbon-carbon unsaturated bond and an electrophilic functional group in the same molecule for intramolecular addition reaction.

16. The process as defined in Claim 15, wherein the intramolecular addition reaction for a compound having a carbon-carbon unsaturated bond and an electrophilic functional group is followed by further addition of a compound having an electrophilic functional group.

17. The process as defined in Claim 15 or 16, wherein the intramolecular addition reaction for a compound having a carbon-carbon unsaturated bond and an electrophilic functional group is followed by addition of an electrophilic reagent.

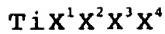
18. The process defined in ~~any of Claims 11 to 17~~, wherein the titanium compound is one which has an asymmetric ligand.

19. The process as defined in ~~any of Claims 11 to 18~~, wherein the compound having a carbon-carbon unsaturated bond is any of olefin compounds, acetylene compounds, or allene compounds.

20. The process as defined in ~~any of Claims 11 to 19~~, wherein the electrophilic functional group is an aldehyde group, ketone group, imino group, hydrazone group, aliphatic double bond, aliphatic triple bond, acyl group, ester group, or carbonate group.

21. The process as defined in ~~any of Claims 11, 12, 14, 17, 18, 19, and 20~~, wherein the electrophilic reagent is water, heavy water, chlorine, bromine, iodine, N-bromosuccimide, oxygen, carbon dioxide gas, or carbon monoxide.

Sub
B3) 22. A process which comprises reacting a titanium compound represented by the formula (1) below



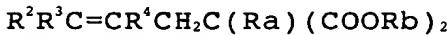
(1)

(where X^1 , X^2 , X^3 , and X^4 denote independently a halogen atom, C_{1-20} alkoxy group, aralkyloxy group, aryloxy group, or $-NR_xR_y$ group (where R_x and R_y denote independently a C_{1-20} alkyl group or aralkyl group), and any two of X^1 , X^2 , X^3 , and X^4 may form a ring.) with a Grignard reagent represented by the formula (2) below in a molar amount 1-10 times as much as the titanium compound,



(2)

(where R^1 denotes a C_{2-10} alkyl group having a hydrogen atom at the β position and X^5 denotes a halogen atom.), thereby forming a titanium catalyst, and deallylating in the presence of the titanium catalyst an allyl-substituted malonate ester derivative represented by the formula (3) below



(3)

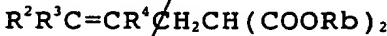
(where R^2 , R^3 , and R^4 denote independently a hydrogen atom or C_{1-10} alkyl group, R_a denotes a C_{1-20} substituted or unsubstituted alkyl group, alkenyl group, or aralkyl group, and R_b denotes a C_{1-10} alkyl group or aralkyl group), thereby giving a malonate ester derivative represented by the formula (4) below



(4)

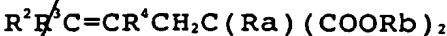
(where R_a and R_b are defined as above).

23. A process which comprises alkylating an allylmalonate ester represented by the formula (5) below



(5)

(where R^2 , R^3 , and R^4 denote independently a hydrogen atom or C_{1-10} alkyl group, and R_b denotes a C_{1-10} alkyl group or aralkyl group), thereby giving an allyl-substituted malonate ester derivative represented by the formula (3) below



(3)

(where R^2 , R^3 , R^4 , and R_b are defined as above, and R_a denotes

a C₁₋₂₀ substituted or unsubstituted alkyl group, alkenyl group, or aralkyl group), reacting this derivative with a titanium compound represented by the formula (1) below



(where X¹, X², X³, and X⁴ denote independently a halogen atom, C₁₋₂₀ alkoxy group, aralkyloxy group, aryloxy group, or -NR_xR_y group (where R_x and R_y denote independently a C₁₋₂₀ alkyl group or aralkyl group), and any two of X¹, X², X³, and X⁴ may form a ring.) and a Grignard reagent represented by the formula (2) below in a molar amount 1-10 times as much as the titanium compound,



(where R¹ denotes a C₂₋₁₀ alkyl group having a hydrogen atom at the β position and X⁵ denotes a halogen atom.), thereby forming a titanium catalyst, and performing deallylating reaction in the presence of the titanium catalyst, thereby giving a malonate ester derivative represented by the formula (4) below



(where Ra and Rb are defined as above).

24. The process as defined in Claim 22 or 23, wherein R², R³, and R⁴ each denote a hydrogen atom.

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Add
β-H

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